



Flame retardant Properties of Polyurethane/expandable Praphite Composites

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Abstract

In an effort to create an environmentally-friendly flame retardant system for rigid polyisocyanurate-polyurethane foams, expandable graphite (EG) combined with aluminum hydroxide (ATH) was firstly used to effectively improve the flame retardancy. Limited oxygen index (LOI) increased to 84.2 with an incorporation of 24 phr (parts per hundred of matrix) EG and 50 phr ATH into the matrix. Based on scanning electronic microscopy observation and thermogravimetric analysis, it was speculated that ATH could effectively induce “villi” like particles on the surface of EG, which made the intumescent char denser. The compact char layer could effectively impede the bubbles and heat transport. ATH and EG accelerated the initial degradation and fluffy char was quickly generated on the surface, which results in the slowed down degradation products of the composite and the delayed diffusion of volatile combustible fragments to flame zone.

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1. Introduction

Nowadays, Polyurethanes have been widely applied in paints, adhesives, elastomers, flexible and rigid foams, etc, and thus play an increasing important role in industry and daily life [1-3]. In the last 30 years, concerns about energy conservation have led to a worldwide use of thermal insulators. In particular rigid polyisocyanurate-polyurethane foams (PIR-PUR) have been widely used for insulation in construction due to their superior mechanical properties and low thermal conductivity. Meanwhile, the increasing public awareness of fire safety of materials, especially those used in construction, has also led to the approval of new regulations [4-6] and wide applications of flame retarded materials. Generally, the flame retardant property of materials could be improved by the incorporation of flame retardants. The common flame retardants used in PIR-PUR are phospho-halogenated compounds. However, those retardants generally cause dense and toxic smokes during burning [7, 8], which inhibit their further development according to the new regulations of fire safety of materials. For these reasons there is an urgent demand to develop effective halogen-free flame retardants for polyurethane foams [9-11].

Intumescent flame retardants (IFRs) are well known as new generation of flame retardants due to their merits, such as low emission of smoke and toxic gases produced during burning and anti-dripping properties [5]. The conventional IFR system is usually composed of three active ingredients, including acid source, blowing agent, and carbon source. Upon heating, these three active ingredients form a multicellular swollen char layer, which slows down the heat and mass transfers

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to interrupt the degradation of a polymer [7-10]. Several new IFR systems have been investigated, such as the pentaerythritol based phosphate system [11], the triazine-rangebased macromolecular charring agent system [12] and expandable graphite (EG) [13, 14].

EG is an intercalated graphite compound in which some oxidants like sulfuric acid and potassium permanganate are inserted between the carbon layers of graphite [15, 16]. When exposed to heat, EG expands and generates voluminous insulating layers, improving flame-retardant properties of the polymeric matrix. The blowing effect causes an increase of the volume of the materials by about 200-250 times on heating above 200 °C. The “worm” like structure developed by graphite expansion suffocates the flame and the intumescent char layer formed limits the heat and mass transfer from polymer to the heat source, preventing further decomposition of the material. However, low efficiency, high loading and high cost still exist, so it is imperative to develop new effective EG systems to reduce fire hazards and meet environmental protection standard for polyurethane foams [14].

Over the last 10 years, researchers have paid great attention to the synergistic effect of organic and inorganic compounds, such as ammonium polyphosphate (APP) [22, 23], triethylphosphate (TEP) [19], red phosphorus (RP) [24] and hydroxide flame retardant [25, 26] in EG systems to enhance the flame retardant efficiency. It was reported that EG and APP could improve the flame retardancy of rigid polyurethane foams [23]. With the incorporation of flame retardant of 15 wt%, the limited oxygen index (LOI) reached 30.5 at a weight ratio of 1:1 for EG and APP. It was attributed to the fact that the phosphoric acid generated from APP has good synergistic effect with EG in improving the char morphology. The char layer hindered the transfer of heat flow and combustible gases in the condensed phase. Modesti and coworkers [24] studied PIR-PUR/EG/TEP composites and found that PIR-PUR/EG (15 wt%) composites showed a LOI value of 25. By incorporating 3 wt% TEP into PIR-PUR/EG (15 wt%) matrix, the LOI value of the composite increased to 34. It was found that TEP and EG in the solid phase could induce a compact char layer, which prevented further decomposition of the underlying material. The effect of RP on the flame retardancy of PIR-PUR/EG systems was also studied by Modesti and coworkers [27]. The fire behavior characterizations demonstrated that the incorporation of RP leads to a substantial improvement of the flame retardancy.

Hydroxide flame retardant [25, 26, 28], such as aluminum hydroxide (ATH), magnesium hydroxide (MH) and layered double hydroxides (LDHs), are cheap, nontoxic and smoke suppressing halogen-free flame retardant additives. The hydroxide flame retardants could also be used as a synergistic agent with EG to enhance the flame resistance of poly(ethylene-vinyl- acetate), polypropylene, etc [25, 26, 28]. However, to the best of our knowledge, there is no public report on the combining effect of hydroxide flame retardant and EG to improve the flame retardancy of PIR-PUR foams. In the present work, the synergistic flame retardant effect of ATH for the EG flame-retarded PIR-PUR composites was reported.

2. Sample preparation and characterization

Unfilled PIR-PURs were prepared by conventional one-pot and free-rise method. Components, such as polyol, catalysts and blowing agent, were mixed together and stirred using an electric stirrer until a uniform mixture was obtained at room temperature. The polyisocyanate was then incorporated in, and the mixture was stirred for an additional 15s. Chemical compositions of the PIR-PUR matrix are shown in Table 1. Then the mixtures were poured into an aluminum cube with a dimension of $250 \times 250 \times 250 \text{ mm}^3$ and containing a paper cup. After that, the foams were placed in an oven at 70 °C for 24 h, in order to complete the polymerization reaction. EG and ATH filled PIR-PUR composites were prepared similarly. EG particles were incorporated into the mixture then. After the EG particles were completely wetted and dispersed in the mixture, ATH and polyisocyanate mixture were incorporated in last. The foam density was normalized to about 0.30 g/cm^3 by varying the dosage of 141b. The composites were prepared with a constant NCO index (300) in order to achieve greater thermal stability and better flame retardant behavior than polyurethane foams.

LOI was used to evaluate the flame retardancy of the PIR-PUR/EG/ATH composites. Specimens with dimension of $130 \times 10 \times 10 \text{ mm}^3$ were used to characterize LOI value using an oxygen index meter (JF-3 Jiangning Analysis Instrument Factory, China) in accordance with ASTM D-2863. The surface morphology of the char was examined by a JSM-6700F field emission Scanning Electron Microscope (SEM) with an operating voltage of 5 kV for this study. 3 mg of sample, taken from the internal region, was used for thermogravimetric analysis (TGA) with a Perkin-Elmer Pyris 1 under N_2 atmosphere with an air flow of 25 mL/min from 50 °C to 750 °C at a heating rate of 20 °C/min.

3. Result and discussion

3.1. flame retardancy

Table 1. LOI results of PIR-PUR/EG composites

EG (phr)	0	4	8	12	16	24
ATH (0phr)	26.5	31.6	35.4	37.3	40.5	47.0
ATH (30phr)	31.1	39.6	44.8	52.6	58.8	65.2
ATH (50phr)	33.8	51.5	58.1	71.5	74.4	84.2

As shown in Table 1, keeping the ATH content at a constant of 0, 30 or 50 phr, different loadings of EG were incorporated into the PIR-PUR composites. Without ATH, the LOI of the PIR-PUR/EG composites improved slightly with increasing the ATH loading, and the 50 phr loading of ATH was necessary to achieve LOI value of 33.8. The LOI increment was only 20.5 with the incorporation of 24 phr EG into the matrix, while the LOI value was 65.2 for PIR-PUR/EG₂₄/ATH₃₀ composites (the subscript number means the loading of flame retardant in the PIR-PUR matrix), and for PUR/EG₀/ATH₃₀, it increased to 31.1 with an improvement of 4.6. Interestingly, the LOI value for the optimized flame retardant PIR-PUR/EG₂₄/ATH₅₀ composites was 84.2, which was 37.2 higher than the PIR-PUR/EG₂₄/ATH₀ composites (LOI=47). It can be included that ATH and EG could synergistically improve the flame retardancy of PIR-PUR. As far as we know, the highest LOI reported of PIR-PUR composites was less than 50 [19, 29, 30].

Table 2. Flame Retardancy of PIR/ATH/EG composites

Samples	TTI (s)	TOF (s)	PHRR (kW/m ²)	MHRR (kW/m ²)	Mass loss (%)	mMLR (g/s)	EHC (MJ/kg)	THR (kW/m ²)
PIR	13	1194	178	75.4	60.9	0.026	25.81	88.53
PIR/ATH30	4	24	155	33.1	47.3	0.030	13.16	19.47
PIR/ATH30/EG8	2	20	142	34.5	46.7	0.024	12.68	20.99
PIR/ATH30/EG16	4	21	118	27.6	38.8	0.021	11.70	18.89

Cone calorimetry was employed to study the flammability properties of these PIR/ATH/EG composites. At present, the cone calorimeter measurement is an efficient means for assessing the fire behavior of materials. The cone calorimeter brings quantitative analysis to the flammability of materials by investigating parameters such as heat release rate (HRR), time to ignition (TTI), and total heat release (THR). The HRR of flame-retardant PIR composites was lower than that of the pure PIR, which was due to the dilution effect of CO₂ and H₂O. The shield effect of expandable graphite could make contribution to the improvement of the flame retardancy. Moreover, EG filled PIR/ATH had lower pHRR. It was explained that the graphite expansion suffocates the flame and the intumescent char layer formed limits the heat and mass transfer from polymer to the heat source, improving the flame retardancy of the composites (Table 2). Because of the low thermal stability of EG and ATH, the flame retardants could catalyze the degradation of PIR, thus the time to ignition decreased to about 2s from 14s of pure PIR (Table 2). Because of the excellent flame retardancy of the composites, time to flame out and THR decreased significantly compared to that of pure PIR.

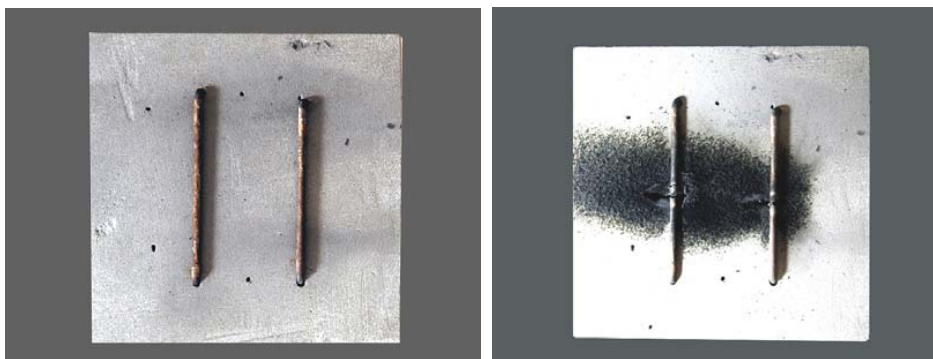


Fig. 1. Photographs of samples before (A) and after (B) burned under acetylene flame

To simulate the thermal shock in the combustion, the high flame retarded PIR-PUR composites were burned under acetylene flame (1300 °C). It was interesting to note that the PIR-PUR composite was only burned slightly while the steel bars placed on the top of PIR-PUR composites had been destroyed, which indicates that the composites have excellent flame retardancy property, as shown in Figure 1.

3.2. Thermal properties

TGA was used to characterize thermal degradation process in terms of mass loss. As shown in Figure 2, it was found that thermal stability of the composites was enhanced with the incorporation of EG. About 21.5 wt% residue was left for pure PIR-PUR foam at 750 °C. The amount of residue improved to 40.2 wt% when 50 phr ATH and 4 phr EG were incorporated and increased to 42.9 wt% when 50 ATH phr and 24 phr EG were incorporated. From the DTG curves, it can be seen that T_{max1} (the temperature for maximum weight loss, i.e., the temperature at the first peak of the derivative TGA curve) decreased 15 °C and the first weight loss rate increased as compared to that of the PIR-PUR matrix, while the second weight loss rate decreased with increasing loading of EG. The reason was that EG and ATH had low thermal stability, thus T_{max1} decreased and weight loss rate increased. After initial degradation, intumescent char generated and the volatile combustible fragments by thermal degradation could slowly diffuse and the weight loss rate decreased. With increasing EG content, denser chars were generated and the weight loss rate decreased further.

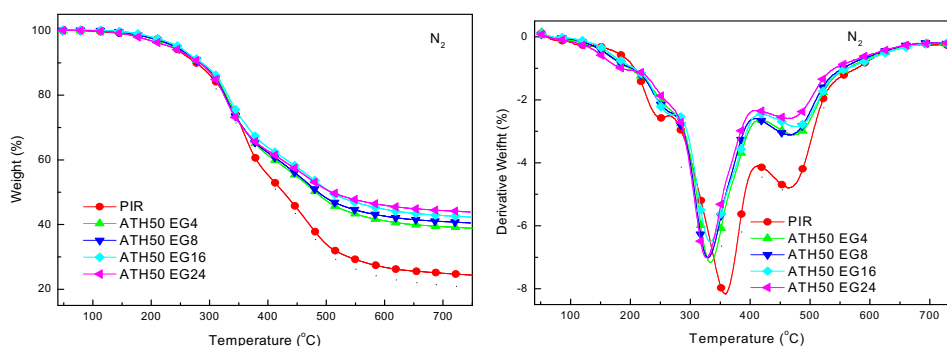


Fig. 2. TGA (left) and DTG (right) curves of PIR-PUR composites

3.3. Morphology of the composites residue chars

The morphology of char influences the flame retardancy and thermal stability of materials greatly during burning. By SEM observation on the residue chars after LOI tests, it was possible to better understand how ATH and EG improved the flame retardancy of the matrix. Figure 3 presents SEM images of the charred layers for PIR-PUR/EG₂₄ and PIR-

PUR/EG₂₄/ATH₅₀ composites. According to Modesti et al [19], the expansion of EG was due to a redox process between H₂SO₄ and the graphite that released the blowing gases, the blowing effect caused an increase of the volume of the materials by about 200-250 times on heating above 200 °C. The “worm” like structure developed by graphite expansion suffocated the flame and the intumescent char layer formed limited the heat and mass transfer from the polymer matrix to the heat source, preventing further decomposition of the materials. According to Huang et al, there are many small holes on the surface of expanded graphite. The size of these holes is about 50 nm to 1 μm [24]. At high magnification [Figure 3(A2)], it can be observed that the surface of expanded graphite was almost smooth. For the char of PIR-PUR/EG₂₄/ATH₅₀ composites, “worm” like structures can be observed at low magnification [Figure 3(B1)]. It is surprising to note that many “villi” like particles were generated on the surface of expanded graphite [Figure 3(B2)]. The particles size was about 100 nm. It was speculated that the “villi” like particles could suffocate the small holes on the surface of expanded graphite, leading to more compact and dense char layers, which could act as a heat insulation barrier and effectively impede the mass transfer of the degraded products between the polymer matrix and burning zone out of the surface. Thus, the generation of volatile combustible fragments by thermal degradation could be slowed down and less combustible products could diffuse to the flame zone, resulting in the improved flame retardancy of the composites.

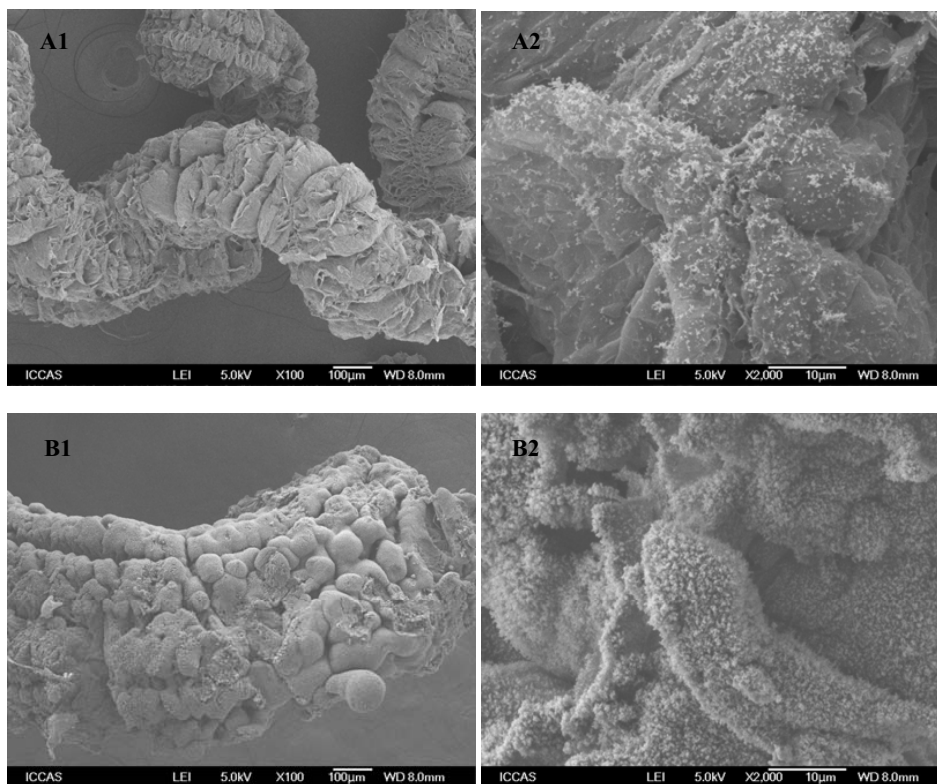


Fig. 3. SEM images of the char layers-- A1 and A2: PIR-PUR/EG₂₄; B1 and B2: PIR-PUR/EG₂₄/ATH₅₀

4. Conclusions

The synergistic effect of EG combined with ATH on flame retardancy of PIR-PUR was investigated systematically in this work. The LOI value of PIR-PUR/EG₂₄/ATH₅₀ composites increased to 84.2 with incorporation of 50 phr ATH and 24 phr EG into the matrix. TGA results indicated that ATH and EG could synergistically accelerate the initial degradation and the quickly form intumescent char could slow down the thermal degradation of volatile combustible fragments and less combustible products diffused into the flame zone. SEM observation showed that ATH could effectively induce “villi” like structure generation on the surface of EG. The “villi” like particles could make the char layers more compact and denser. This kind intumescent char layer could act as a heat insulation barrier and effectively impede the mass transfer of degraded products between the polymer matrix and burning zone, resulting in the enhanced flame retardancy for PIR-PUR.

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